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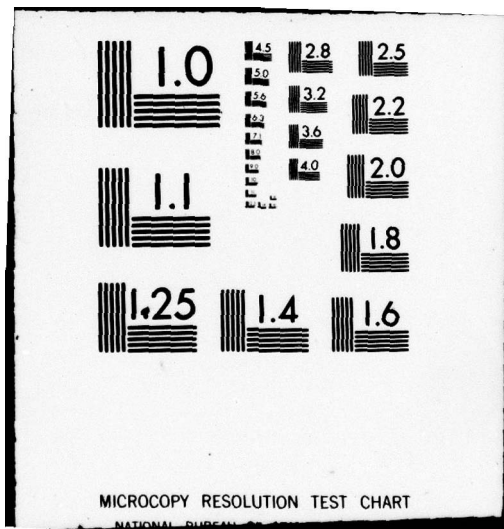
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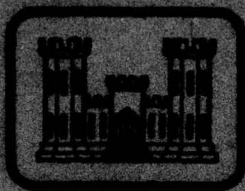


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THE 7.6-ANGSTROM REACTION PRODUCT IN SMECTITE CLAY-LIME MIXTURES

by

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20. ABSTRACT (Continued)

carbonate-11 hydrate (monocarboaluminate).

The type of exchangeable cation in the clay had no effect on the reaction. On the other hand the presence of magnesium rather than aluminum in the octahedral layer of the clay mineral hectorite prevented the usual reactions because these mixtures never hardened.

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PREFACE

This work was funded by Department of the Army Project No. 4A061101A91D, Item DL, "In-House Laboratory Independent Research Program," sponsored by the Assistant Secretary of the Army (R&D).

Funds for the publication of this report were provided from those made available for operation of the Concrete Technology Information Analysis Center (CTIAC). This is CTIAC Report No. 41.

The work was conducted in the Concrete Laboratory (CL) of the U. S. Army Engineer Waterways Experiment Station (WES) under the direction of Messrs. Bryant Mather and Leonard Pepper, and Mrs. Katharine Mather, during the period 1 July 1974 through 30 September 1977. COL G. H. Hilt, CE, was project leader during his stay at WES. Mrs. Mather then took over as project leader. She and Mr. A. D. Buck prepared this report.

A presentation based on this work was made at the Joint Conference of the Clay Minerals Society and the International Committee for the Study of Bauxites, Alumina, and Aluminum in Kingston, Jamaica, during 1977.

The assistance of Dr. John W. Jordan, Baroid Division, National Lead Industries, and Dr. L. E. Copeland of Wiss, Janney, Elstner and Associates, is gratefully acknowledged. Dr. Jordan supplied the hecto-rite clay that was used and Dr. Copeland made a limited examination of the 7.6-Å reaction product with an electron probe.

The Commanders and Directors of WES during the conduct of this project and publication of this report were COL G. H. Hilt, CE, COL J. L. Cannon, CE, and COL N. P. Conover, CE. Mr. F. R. Brown was Technical Director.

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CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
inches	0.0254	metres
inches	25.4	millimetres
pounds (force) per square inch	0.00689476	megapascals
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain Kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$.

(12) THE 7.6-ANGSTROM REACTION PRODUCT
IN SMECTITE CLAY-LIME MIXTURES

PART I: INTRODUCTION

1. In his thesis,¹ George H. Hilt provided data on a crystalline reaction product he had found in clay-lime, soil-lime, and fly ash-lime mixtures. Its longest and strongest X-ray spacing was at about 7.6 Å. He indicated that the material was similar to C_4AH_{13} * and that it might be C_4AH_{13} or a form of it that included silica or carbonate ions. The work reported herein was done to extend his findings. It was hoped that it would be possible to grow larger single crystals of the crystalline reaction product than he had grown. This work fits into the entire study of soil stabilization and the chemical reactions that occur during hardening of soil, lime, and water mixtures.

* $C = CaO$, $A = Al_2O_3$, $H = H_2O$, $\bar{C} = CO_2$.

PART II: MATERIALS, MIXTURES, AND PROCEDURES

2. The intent was to use materials and mixtures generally similar to those Hilt¹ had used to minimize experimentation and to insure that the desired reaction product was obtained.

3. The following three smectites* were used:

- a. WES-45 CL-1. This material is "Volclay" from the American Colloid Co. The source is probably the Black Hills of South Dakota. This material contains sodium as its principal interlayer exchangeable cation.
- b. WES-45 CL-2. This material is Panther Creek Southern bentonite, also from the American Colloid Co. It is from White Springs, Mississippi. It contains calcium as its principal interlayer exchangeable cation.
- c. WES-45 CL-3. This material is purified hectorite from near Hector, California. It contains sodium as its main interlayer exchangeable cation but differs from the other smectites used in that it contains magnesium rather than aluminum as a principal constituent of the octahedral portion of the clay structure.

4. The intent of using the different kinds of smectites was to determine if their differences affected the desired reaction product.

5. Fly ash from Wilsonville, Alabama, was used in some mixtures. It is identified as WES-283 F-74.

6. Reagent-grade $\text{Ca}(\text{OH})_2$ was used as lime in the mixtures. It was not assigned a serial number.

7. Reagent-grade CaCO_3 was used in some mixtures. It was not assigned a serial number.

8. Each of these six materials was examined by X-ray diffraction for purity and to determine its composition.

9. Distilled water was used in all mixtures.

10. Trial mixtures were made with the Volclay and the Panther Creek smectites. These contained 20 percent of lime by weight of clay and a water to total solids ratio of 1.40, 1.50, 1.75, and 2.50 for the Volclay and 0.80, 0.90, and 1.00 for the Panther Creek smectite. No

* Montmorillonitic clay.

calcite was used. These mixtures were placed in plastic containers with snap-on lids. Containers of each mixture were stored at 40 to 44°F* and others were kept at room temperature (about 73°F) in a moist cabinet. X-ray diffraction examinations of portions of these mixtures were made periodically for about 6 months. The X-ray results indicated that these mixtures needed more lime.

11. Additional mixtures were made with each of the three smectites and the fly ash using 100 g of clay or fly ash, 70 g of lime, 13 g of calcite, and 183 g of water. The 183 g of water was not enough to produce plastic mixtures with the Volclay and the hectorite. After experimentation to find a better water content for these two clays, mixtures were made with 320 g of water for the Volclay and 750 g of water for the hectorite. The amounts of clay or fly ash, lime, and calcite were intended to furnish about 0.16 moles of Al_2O_3 (except for the hectorite), 0.95 moles of $\text{Ca}(\text{OH})_2$, and 0.13 moles of CaCO_3 , respectively. These proportions were selected to give a $\text{C}_3\text{A}/\text{CaCO}_3$ ratio of about 0.8 and a $\text{Ca}(\text{OH})_2/\text{C}_3\text{A}$ ratio of about 1. This was done to promote growth of the 7.6-Å reaction product and is based on data from Seligmann and Greening.² All of these mixtures were placed in sealed plastic containers. Each mixture was divided for storage at 50°F and at room temperature (about 73°F) in a moist cabinet. Specimens from the mixtures were X-rayed periodically as before. When little or no reaction of the 50°F samples was detectable by X-ray diffraction after 3 months time, all specimens were placed in the room temperature moist cabinet.

12. Each of the mixtures was X-rayed by grinding a small portion and packing the wet material into a sample holder so it was examined while it was wet.

13. When the second group of mixtures was about 15 months old the containers were examined with a stereomicroscope for the presence of new crystals that would serve as seed crystals to grow larger single crystals. It was found that many small crystals of the desired

* A table of factors for converting U. S. customary units of measurements to metric (SI) units is presented on page 3.

appearance were detectable on dried surfaces that had been formed by contact of a mixture with a container surface.

14. After a check for purity of $C_{12}A_7$ by X-ray diffraction a saturated solution of $C_{12}A_7$ was prepared as a nutrient solution to use in growing larger single crystals of the reaction product. Individual crystals from the Panther Creek smectite mixture were placed in this nutrient solution. These crystals were obtained with a dissecting needle from formed surfaces while observing with a stereomicroscope at 125X. Since the single crystals were not visible when placed in the nutrient solution and did not grow to a visible size, small fragments of the mixture containing many small crystals were placed in the nutrient solution. Some of these solutions with their samples were kept at room temperature, others were stored at 50°F, and others at about 120°F to see if these temperature extremes would promote crystal growth.

15. When it became apparent that those efforts were not going to result in the desired enlarged single crystals, several of the available crystals were carefully removed from a dried surface of a Panther Creek smectite-lime mixture. These crystals were ground in alcohol and this slurry was allowed to dry on a small glass slide. The dried surface of this slide was then examined by X-ray diffraction to obtain an X-ray pattern of as pure a sample of these crystals as was obtainable.

16. Since there was an interest in possible chemical substitution in the structure of this reaction product, a sample of a Panther Creek smectite-lime mixture containing added quartz was examined by X-ray diffraction. The 3.34-Å quartz peak was used as an internal standard to determine what the true position of the 7.6-Å peak of the reaction product should be. It was assumed that chemical substitution would cause displacement of the 7.6-Å peak.

17. A few of the crystals of the 7.6-Å reaction product were made into powder immersion mounts and examined with a polarizing microscope to determine optical properties.

18. A formed surface of a dried fragment of the Panther Creek smectite-lime mixture was coated with a layer of carbon and then with a layer of Ag-Pd metal. This surface was examined with a scanning

electron microscope (SEM) and several scanning micrographs were taken of the crystals of interest.

19. A sample of the Panther Creek smectite-lime mixture was furnished to Dr. L. E. Copeland. He examined some of the 7.6-Å crystals on the surface of this sample with an electron probe to determine if chemical substitution could be detected.*

20. Compressive strength data were obtained by breaking crude cubes from the high lime mixtures made with the Volclay, the Panther Creek, and with the fly ash materials at ages of about 3 months and 15 to 18 months. The cubes were obtained by cutting them from the mixtures with a diamond saw.

21. All X-ray patterns were made with an X-ray diffractometer using nickel-filtered copper radiation.

* Personal communication.

PART III: RESULTS

22. The objective of growing large crystals to do analytical work on individual crystals was not achieved. Individual tabular crystals about 250 μm wide by about 25 μm thick were the largest that were obtained. Therefore, most of the work on the crystals was done on a composite sample made up of many hand-picked single crystals. These are believed to be like those grown by Hilt.¹

23. Chemical and physical data for the three smectites and the fly ash are shown in Table 1; the lack of aluminum in the hectorite is apparent.

24. X-ray data suggest that the Volclay is about 90 percent smectite with a trace of kaolinite, and 10 percent quartz, cristobalite, and tirdymite; the Panther Creek material is about 90 percent smectite with a trace of clay-mica, and 10 percent quartz, tirdymite, feldspar, and calcite; the hectorite is largely smectite with small amounts of calcite and dolomite; there may also be a little clay-mica and serpentine in it. The fly ash is largely glass with small amounts of quartz, mulite, hematite, and magnetite.

25. X-ray examination indicated that the calcium hydroxide and the calcite were essentially pure.

26. The observations made by periodic X-ray examination of the mixtures are given below:

- a. Two detectable crystalline reaction products were found in the clay-lime mixtures containing Volclay and Panther Creek smectites. They were characterized by X-ray spacings at 8.2 and 7.6 \AA . Storage at temperatures between 44 and 50°F favored formation of the 8.2- \AA compound. However, with additional time and storage at room temperature (about 73°F), the 7.6- \AA material was more common. These peaks were sometimes detectable after storage periods of about 30 days.
- b. The probability that the 8.2- \AA material is a reaction product is complicated by the fact that the smectites would be expected to have a second order X-ray reflection at about that value. However, the sharpness of the 8.2- \AA peak is believed to be adequate evidence that it is, in part, at least, a reaction product.

- c. There was no detectable 7.9-Å reaction product. This would be characteristic of C_4AH_{13} . It should not occur since there was enough carbonate present to favor the formation of other compounds.
- d. No reaction products were found in the hectorite smectite-lime mixtures. Further evidence of a lack of reaction was the fact that these mixtures did not develop measurable compressive strength. They were still soft to the touch at an age of about 20 months. The crystallinity of the hectorite seemed unaffected as judged by X-ray diffraction patterns.
- e. The crystallinity of the Volclay and Panther Creek smectite X-ray peaks seemed unaffected after 6 months of storage. However their X-ray peaks indicated a definite decrease in crystallinity by an age of about 20 months.
- f. Calcium hydroxide and calcite peaks were still present in the high lime mixtures after 20 months of storage.
- g. In addition to 8.2- and 7.6-Å compounds, the fly ash-lime mixtures also showed X-ray peaks that indicated the presence of ettringite. The 8.2-Å peak was always stronger than the 7.6-Å peak; this indicates a reversal of what was found in the clay-lime mixtures.
- h. The amounts of detectable 8.2- and 7.6-Å reaction products appeared to be similar in the Volclay and Panther Creek smectite-lime mixtures at the same water contents.

27. Examination with a stereomicroscope of dried portions of the mixtures, especially the surfaces formed by contact with the plastic surfaces of the containers, showed an abundance of small, transparent, tabular crystals. This examination was best made at 100 to 125X. A partial list of the X-ray spacings obtained from a composite sample of these crystals is shown in Table 2. Spacings for calcium monocarboaluminate ($C_4A\bar{C}H_{11}$) and for the reaction product Hilt¹ found are also shown for comparison. All of these X-ray patterns appear to be essentially the same. The fact that the present crystals are the same 7.6-Å reaction product found in the X-ray patterns of the whole mixtures shows that they are the material that was intended to be studied. The use of quartz as an internal standard indicated that the correct spacing of the 7.6-Å reaction product was 7.57 Å. Thus, no chemical substitution was indicated by the X-ray data.

28. Portions of the formed surface of the Panther Creek smectite-

lime mixture that were examined by SEM are shown in Photos 1-6. These show the appearance of the 7.6-Å crystals at magnifications ranging from 330 to 5200X. Photos 1 and 3 show that the crystals appear to be deformed hexagons.

29. Examination of some of the 7.6-Å crystals as powder immersion mounts with a polarizing microscope showed the following:

- a. The crystals are biaxial negative. Therefore, they do not fall in the hexagonal system.
- b. The birefringence was low with a refractive index close to 1.557. Some of the crystals tended to disappear in the immersion oil at or near this value. Due to their tabular shape only the refractive indices seen on flat lying crystals were checked.

30. It has been reported³ that $C_4\bar{A}CH_{11}$ forms colorless, hexagonal plates with refractive indices of $N_o = 1.552$ and $N_e = 1.532$. The comparison of optical data between $C_4\bar{A}CH_{11}$ and the 7.6-Å crystals grown in this work fails to show precise agreement even though X-ray diffraction data indicate that the 7.6-Å material is $C_4\bar{A}CH_{11}$. This indicates either that the data in the reference are in error, our data are in error, or that $C_4\bar{A}CH_{11}$ has a range in optical properties.

31. In addition to limiting the optical data that were obtainable, the predominantly tabular shape of the 7.6-Å crystals caused the X-ray diffraction patterns to show strong preferred orientation of some peaks.

32. Compressive strength data are shown in Table 3 for the Volclay, Panther Creek, and fly ash-lime mixtures. These data show an increase of strength with time for all mixtures and a decrease in strength with increasing water content for the Volclay mixtures. The others were made with a single water content. The fly ash-lime mixture is about six times stronger than the clay-lime mixtures at matching ages. The strengths of the two smectite mixtures are similar at equal ages and similar water contents. X-ray diffraction data for the 3-month-old mixtures and the 15- to 18-month-old mixtures shown in Table 3 show more 7.6-Å material with increasing strength for the two smectites. However, the amounts of 7.6-Å material are about equal for the fly ash mixtures having substantially different strengths. It is not clear

tion product is contributing to the solution of the problem.

PART IV: DISCUSSION

33. When Hilt¹ was working with his mixtures and trying to identify the 7.6-Å material, the crystalline products of these reactions were relatively unknown and there was confusion about the identification of hydrated calcium aluminates. Since that time, Diamond and Kinter⁴ reviewed soil-lime reactions. They pointed out that a calcium silicate hydrate and a calcium aluminum hydrate are produced by these reactions. They also said the latter is a hexagonal compound which is probably an impure tetracalcium aluminate hydrate that is characterized by a 7.6-Å X-ray diffraction spacing.

34. A considerable amount of other work⁵⁻¹¹ has been done to sort out the different forms of hydrated calcium aluminates, largely in relation to portland cement. There is now general agreement about the identity of the varieties of hydrated calcium aluminates which is based on the position of the longest X-ray spacing. A spacing of 7.9 Å characterizes C_4AH_{13} whereas 8.2- and 7.6-Å spacings signify the presence of hemicarboaluminate ($C_4\bar{A}\bar{C}_{0.5}H_{12}$) and monocarboaluminate ($C_4\bar{A}\bar{C}H_{11}$), respectively. All of these are members of the AFm group of hydrated calcium aluminates. Schwiete and Ludwig⁶ said they are hexagonal or pseudo-hexagonal sheets in which the water of crystallization is bound in layers normal to the C-axis. Taylor¹¹ says the layers of materials in the AFm group pack together to leave cavities which may contain different anions. For carbonate-bearing phases no significant change of the C-axis spacing occurs with changes in the alumina to iron ratio.¹¹ Dosch, Keller, and Zur Strassen⁷ state about these materials that a certain low amount of embedded anions is sufficient to produce a characteristic basal spacing and further exchange of one kind of anion for another probably only influences the crystal symmetry. The gist of it all is that the AFm type of structure can accommodate foreign ions. However, Dr. L. E. Copeland* did not detect any silica in the 7.6-Å crystals that he examined with an electron probe. It had been thought that this was a likely candidate for inclusion in that lattice.

* Personal communication.

35. Thus, in the present work we have reaction products characterized by X-ray spacings at 8.2 and 7.6 Å. Based on modern data,⁵⁻¹¹ it would seem that these should be calcium hemicarboaluminate ($C_4\bar{A}\bar{C}_{0.5}H_{12}$) and calcium monocarboaluminate ($C_4\bar{A}\bar{C}H_{11}$),¹² respectively. The kind of exchangeable cation in the smectite did not have any detectable effects on the reaction products that were developed. The presence of magnesium rather than aluminum in the octahedral layer of the hectorite effectively prevented the formation of any hydrated calcium aluminates since there was no other source of aluminum. Since there was no cementation of the hectorite-lime mixtures at 20 months age the implication is that the usual formation of hydrous calcium silicate was also inhibited by this chemical and structural form of smectite. This finding could perhaps explain some instances where a soil-lime mixture does not harden as expected.

36. The X-ray data indicate that the 7.6-Å material produced in the present work is the same material that was produced by Hilt¹ and that this is $C_4\bar{A}\bar{C}H_{11}$ (Table 2). Since the optical data indicate the 7.6-Å crystals are not hexagonal (i.e., uniaxial negative) and have slightly higher refractive indices than published values³ for $C_4\bar{A}\bar{C}H_{11}$, this discrepancy needs consideration. In addition, Hilt¹ reported that his crystals were uniaxial negative and had an index of refraction of about 1.548, so his refractive index is intermediate to those for $C_4\bar{A}\bar{C}H_{11}$. It is believed that the likely explanation is that there has been enough chemical substitution, not by silica, into the $C_4\bar{A}\bar{C}H_{11}$ lattice to effect slight changes in the optical properties of the 7.6-Å material without causing detectable modification of the X-ray pattern. The same type of explanation may apply to Hilt's¹ 7.6-Å crystals since their refractive indices also differ from those for $C_4\bar{A}\bar{C}H_{11}$.³

37. It is postulated that $C_4\bar{A}\bar{C}H_{11}$ and $C_4\bar{A}\bar{C}_{0.5}H_{12}$ are normal crystalline reaction products for most soil or clay or fly ash and lime mixtures. They form instead of $C_4\bar{A}H_{13}$ because carbonate is almost always available either in the form of calcite or as CO_2 in air or water. It appears that the 8.2-Å $C_4\bar{A}\bar{C}_{0.5}H_{12}$ probably forms first and tends to convert to the 7.6-Å $C_4\bar{A}\bar{C}H_{11}$ if enough carbonate is available. In those

rare cases where no CO_2 might be present the calcium aluminate would probably be the $7.9\text{-}\overset{\circ}{\text{A}}$ C_4AH_{13} form or one with higher or lower water content; this would depend on the environment during formation and during the examination.

PART V: CONCLUSIONS

38. The 7.6-Å material in clay-lime mixtures examined by Hilt¹ and as part of the present work is calcium monocarboaluminate hydrate ($C_4\bar{A}\bar{C}H_{11}$) with the material examined here chemically different enough to affect the optical but not the X-ray data.

39. The crystalline hydrated calcium aluminates $C_4\bar{A}\bar{C}_{0.5}H_{12}$ and $C_4\bar{A}\bar{C}H_{11}$ are to be expected as normal reaction products of most clay or soil, water, and lime mixtures at nonextreme temperatures. The first material is characterized by an 8.2-Å X-ray diffraction spacing and the second material by a 7.6-Å X-ray diffraction spacing.

40. Since the fly ash and lime mixture also contained ettringite ($C_6\bar{A}\bar{S}_3H_{32}$) in addition to $C_4\bar{A}\bar{C}H_{11}$ and $C_4\bar{A}\bar{C}_{0.5}H_{12}$, other such mixtures may also contain these crystalline reaction products.

41. The type of exchangeable interlayer cation in the smectite clay does not appear to affect the X-ray diffraction spacings of the 7.6-Å reaction product that is formed nor its amount. On the other hand the data show that if smectite contains magnesium rather than aluminum in its octahedral layer (i.e., hectorite) the usual clay-lime reactions do not occur, at least not up to 20 months age which was the limit in the present work. This lack of reaction with subsequent failure to develop measurable compressive strength could explain some instances in the field when soil-lime mixtures fail to develop strength as expected. Hectorite is a fairly rare clay mineral.

REFERENCES

1. Hilt, G. H., "Isolation and Investigation of a Lime-Montmorillonite Reaction Product," Ph. D. thesis, Iowa State University, Ames, Iowa, 1961.
2. Seligmann, P., and Greening, N., "Phase Equilibria of Cement-Water," Proceedings of the 5th International Symposium on Cement and Concrete, Tokyo, Vol 2, 1968, pp 179-200.
3. Winchell, A. N., and Winchell, H., "The Microscopical Characters of Artificial Inorganic Solid Substances: Optical Properties of Artificial Minerals," Academic Press, New York, 1964, p 86.
4. Diamond, S., and Kinter, E. B., "Mechanisms of Soil-Lime Stabilization: An Interpretive Review," Public Roads, Vol 33, No. 12, Feb 1966, pp 260-265 and 273.
5. Seligmann, P., and Greening, N. R., "New Techniques for Temperature and Humidity Control in X-Ray Diffractometry," Portland Cement Association Journal of the R and D Laboratories, Vol 4, No. 2, May 1962, pp 2-9.
6. Schwiete, H. E., and Ludwig, V., "Crystal Structures and Properties of Cement Hydration Products (Hydrated Calcium Aluminates and Ferrites)," Proceedings of the 5th International Symposium on Cement and Concrete, Tokyo, Vol 2, 1968, pp 37-67.
7. Dosch, W., Keller, H., and Zur Strassen, H., Discussion of above item, pp 72-76.
8. Roberts, M. H., "Calcium Aluminate Hydrates and Related Basic Salt Solid Solutions," Proceedings of the 5th International Symposium on Cement and Concrete, Tokyo, Vol 2, 1968, pp 104-117.
9. Ahmed, S. J., Dent Glasser, L. S., and Taylor, H. F. W., "Crystal Structures and Reactions of C_4AH_{12} and Derived Basic Salts," Proceedings of the 5th International Symposium on Cement and Concrete, Tokyo, Vol 2, 1968, pp 118-127.
10. Ariizumi, A., "Formation of Hydrated Gehlenite Through the Reaction of Clay Minerals and Lime," Proceedings of the 5th International Symposium on Cement and Concrete, Tokyo, Vol 2, 1968, pp 138-147.
11. Taylor, H. F. W., "Crystal Chemistry of Portland Cement Hydration Products," Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow, 1974.
12. Highway Research Board, "Guide to Compounds of Interest in Cement and Concrete Research," Special Report 127, 1972, Washington, D. C.

Table 1

Chemical and Physical Data for Three Smectite Clays and a Fly Ash

Chemical Data, Percent	WES-45 CL-1		WES-45 CL-2		WES-45 CL-3		WES-283 F-74 Fly Ash
	Volclay*	Panther Creek*	Purified Hectorite**				
SiO ₂			53.6				
Al ₂ O ₃			0.9				90.4
Fe ₂ O ₃			0.3				
MgO			26.5				1.5
CaO			0.1				
Na ₂ O			2.6				
K ₂ O			0.2				
LiO ₂			1.0				
SO ₃			not deter- mined				0.3
Loss at 105°C			8.2				
Loss at 900°C			5.2				
Available alkalies			not deter- mined				0.6
Exchangesable cations,† meq/100 g							
Ce	20.9	64.1	14.6				
Mg	11.8	13.0	11.0				
Na	52.2	0.7	79.7				not deter- mined
K	1.3	1.0	1.6				
Total	86.2	78.8	106.9				
Cation exchange capacity,† meq	67.1	61.5	78.3				

(Continued)

Table 1 (Concluded)

Physical Data	WES-45 CL-1 Volclay*	WES-45 CL-2 Panther Creek*	WES-45 CL-3 Purified Hectorite**	WES-283 F-74 Fly Ash
Specific gravity	2.29	2.19	2.30	2.23
Surface area (Blaine), cm ⁻¹	3250	5450	--	8250
Range	--	--	7270-10,420	--
Average	--	--	8720	--

* No chemical analysis was made.

** Surface area results were not reproducible.

+ Extraction with ammonium acetate at pH 7. Method of H. D. Chapman in Methods of Soil Analysis, Part 2, American Society of Agronomy, Inc., Madison, Wis., 1965.

Table 2
Comparison of X-Ray Diffraction Data - 7.6-Å Material

Present Work*		ASTM Card 14-83**		Hilt [†]		Comment
A	I	A	I	A	I	
10.6	vw					May be noise
9.4	vw					
9.1	vw					
7.57	vs	7.59	100	7.59	10	
		4.36	6			
		3.99	6			
3.77	vs	3.78	45	3.85	7	
		3.66	2			
3.45	vw	3.46	6	3.42	4	
3.34	vw					
2.84	vw	2.86	30	2.87	9	
2.77	vw	2.78	8			
2.71	vw	2.72	14	2.71	1	
2.65	vw	2.65	4			
2.51	m	2.52	18	2.52	6	
2.49	vw	2.49	18			
2.41	w	2.42	25			
2.33	w	2.34	20	2.33	6	
2.28	vw	2.29	4	2.30	8	
		2.24	4			
				2.20	4	
2.15	vw	2.17	6			
2.11	vw	2.12	8	2.11	5	
2.08	w	2.10	6	2.07	1	
		2.07	2			
2.02	vw	2.02	2			
2.00	vw	2.01	6			
1.94	w	1.94	10	1.93	3	
1.91	vw	1.91	2			
1.89	w	1.89	4			
1.87	vw	1.86	8	1.86	3	
†		†		†		

* Composite of hand-picked crystals.

** Joint Committee on Powder Diffraction Standards, Powder Diffraction File, Set 14, 1964.

† Each pattern contains additional lines.

Table 3

Compressive Strength of Clay-Lime and Fly Ash-Lime Mixtures at Two Ages*

Specimen Age	Water Content, g per 183 g of Solids	Compressive Strength, psi		
		Volclay (WES-45 CL-1) Plus Lime	Panther Creek (WES-45 CL-2) Plus Lime	Fly Ash (WES-283 F-74) Plus Lime
About 3 months	320	40	**	**
	183	**	110	650
15 - 18 months	320	130	**	**
	230	360	**	**
	183	370	360	2140

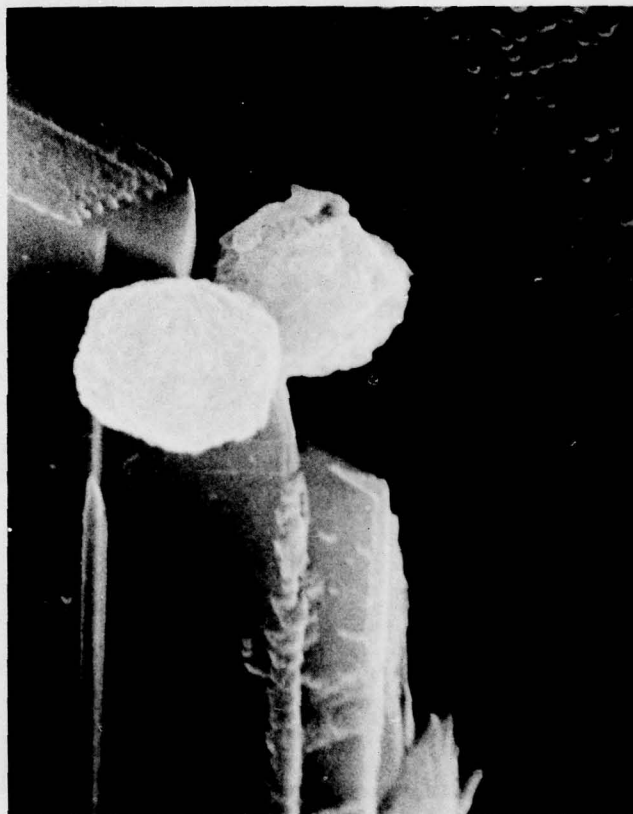
* Each value is an average for several nominal 1-in. sawed cubes.

** No specimens at this water content.



Typical crystal growth on formed surfaces of Panther Creek smectite-lime mixture, X330. Age of mixture is about 14 months. The arrow points to the area shown in the next picture. Negative 06 09 76-5.

Photo 1. SEM photomicrograph 1



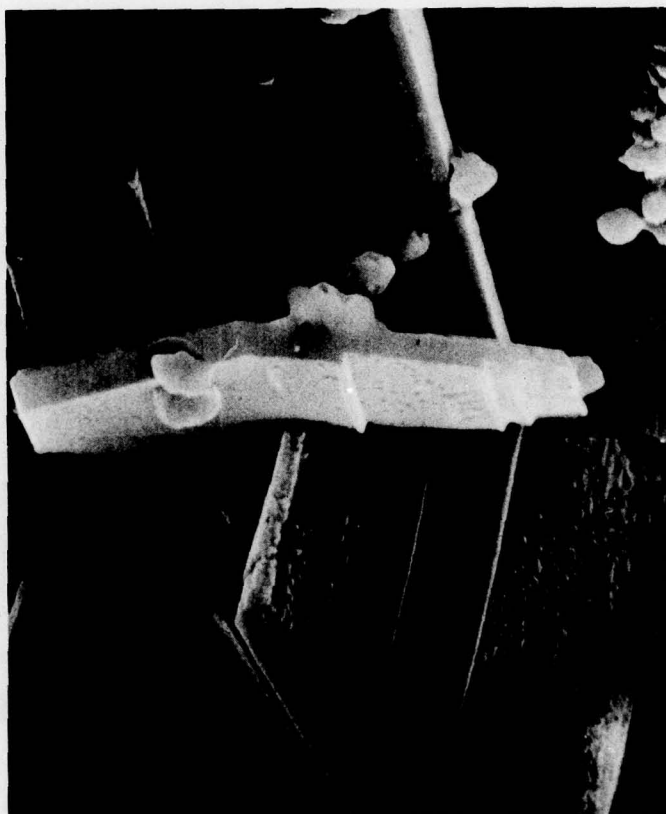
Enlargement of area indicated by arrow in previous photo, X5200. The two white spherical objects are secondary calcium carbonate found associated with most of these crystals. Negative 06 09 76-6.

Photo 2. SEM photomicrograph 2



Another area of typical crystal growth, X370,
on the same specimen as SEM photomicrograph 1.
The arrow points to area shown in the next
picture. Negative 06 09 76-9.

Photo 3. SEM photomicrograph 3



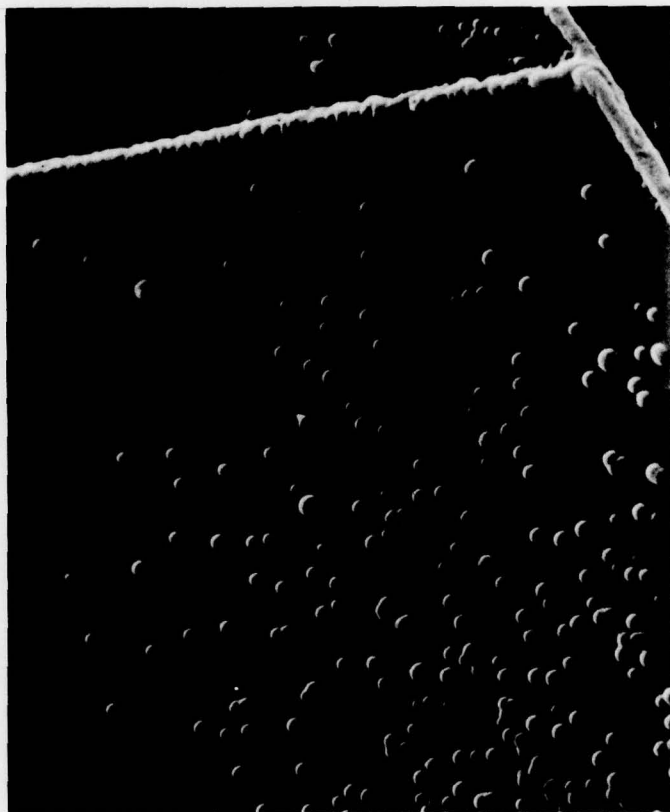
Enlargement of area indicated by arrow in previous photo, X2000. Illustrates complex crystal intergrowth and stair-stepped surfaces. Negative 06 09 76-11.

Photo 4. SEM photomicrograph 4



A third area of crystal growth on the same specimen as SEM photomicrograph 1, X500. The crystals in the lower right appear less tabular than usual. The arrow points to the area shown in the next photo. Negative 06 09 76-41.

Photo 5. SEM photomicrograph 5



Enlargement of area indicated by arrow in previous photo, X5000. Many crystals show entrapped bubbles such as these. Negative 06 09 76-38.

Photo 6. SEM photomicrograph 6

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Buck, Alan D

The 7.6-angstrom reaction product in smectite clay-lime mixtures / by Alan D. Buck, Katharine Mather. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1979.

18, [10] p. : ill. ; 27 cm. (Miscellaneous paper - U. S. Army Engineer Waterways Experiment Station ; SL-79-22)

Prepared for Assistant Secretary of the Army (R&D) Department of the Army, Washington, D. C., under Project No. 4A061101A91D, Item DL.

CTIAC Report No. 41.

References: p. 18.

1. Carboaluminates. 2. Chemical reactions. 3. Clay-lime reactions. 4. Soil stabilization. 5. X ray diffraction. I. Mather, Katharine, joint author. II. United States. Assistant Secretary of the Army (Research and Development). III. Series: United States. Waterways Experiment Station, Vicksburg, Miss. Miscellaneous paper ; SL-79-22.

TA7.W34m no.SL-79-22